PATENT SPECIFICATION

1,113,925

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NO DRAWINGS

Inventor: BRION WELLER

Date of filing Complete Specification: 24 Aug., 1965.

Application Date: 18 Sept., 1964. *No. 38127/64.*

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Index at acceptance:—C3 R(32D6A, 32E2, 32E9, 32F5, 32G2, 32H5F, 32H8, 32J1, 32J2A, 32J2Y, 33P); B2 E(1A, 1H)

Int. Cl.:—C 08 g 21/02

SEE ERRATA SLIP ATTACHED

COMPLETE SPECIFICATION

Polyurethane Pressure-Sensitive Adhesives

... of attachment of a chain

ERRATA

SPECIFICATION No. 1,113,925

Page 1, line 36, *for* "stoichiometric" *read* "stoichiometrical"

Page 2, line 80, *for* "triphenylmethyl" *read* "triphenylmethane"

Page 4, Example III, *for* "diisocyanatadiphenylmethane" *read* "diisocyanatodiphenylmethane"

Page 6, line 27, *for* "glycerol" *read* "glycol"

THE PATENT OFFICE
18th June 1968

a method of preparing a pressure-sensitive adhesive comprises reacting one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and the stoichiometrical amount of an organic polyisocyanate, the hydroxyl-containing compounds being in sufficient proportions dependent on their molecular weights to produce a fully cross-linked reaction product with said polyisocyanate, said reaction product having an average chain-length of from 130 to 285 chain-atoms.

The stoichiometric amount of an organic polyisocyanate is the amount of said polyisocyanate required to react with all the hydroxyl groups of the polyols, diols and monols in order to produce a fully cross-linked reaction product.

By the term "chain-length" as used in this Specification there is meant the length of a chain in terms of chain-atoms as measured

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light pressure is applied ... tures in the absence of heat, moisture and other agents.

The polyols employed in this invention may be hexols, e.g. sorbitol, pentols, e.g. arabitol, tetrols, e.g. pentaerythritol, or triols, e.g. glycerol. Also, reaction products of these polyols and propylene oxide and/or ethylene oxide may be used in place of the unmodified polyols, the preferred triol being a reaction product of glycerol and propylene oxide. Examples of diols which can be employed are poly(ethylene glycol) and poly(propylene glycol) which is the preferred diol. Examples of mono-ols which can be used are methyl oxitol and *n*-butanol.

Various combinations of hydroxyl-containing compounds, i.e. mono-ols, diols, triols, etc., can be employed in this invention, for instance, a single kind of tetrol or triol, mixtures of different tetrols and/or triols having different molecular weights, mixtures of

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COMPLETE SPECIFICATION

Polyurethane Pressure-Sensitive Adhesives

We, THE DUNLOP COMPANY LIMITED, formerly Dunlop Rubber Company Limited, a British Company of Dunlop House, Ryder Street, St. James's, London, S.W.1., formerly of 1, Albany Street, London, N.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pressure-sensitive adhesives and to a method of making them.

According to the present invention, a pressure-sensitive adhesive comprises a fully cross-linked reaction product of one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and an organic polyisocyanate, said reaction product having an average chain-length of from 130 to 285 chain-atoms.

According to the present invention also, a method of preparing a pressure-sensitive adhesive comprises reacting one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and the stoichiometrical amount of an organic polyisocyanate, the hydroxyl-containing compounds being in sufficient proportions dependent on their molecular weights to produce a fully cross-linked reaction product with said polyisocyanate, said reaction product having an average chain-length of from 130 to 285 chain-atoms.

The stoichiometric amount of an organic polyisocyanate is the amount of said polyisocyanate required to react with all the hydroxyl groups of the polyols, diols and monols in order to produce a fully cross-linked reaction product.

By the term "chain-length" as used in this Specification there is meant the length of a chain in terms of chain-atoms as measured from the point of attachment of a chain branching therefrom, to an adjacent point of attachment of a further chain branching from the first-mentioned chain, or as measured from the point of attachment of a chain branching from the first-mentioned chain to the end of the first-mentioned chain if the first-mentioned chain is free from attachments at one end.

The term "chain-atoms" refers only to the atoms in the main chain and does not include branch-chain atoms.

Preferably, the reactants are applied in a liquid state to a substrate such as a paper or cloth fabric or a thin plastics sheet, whereon they react to form a pressure-sensitive adhesive.

By a "pressure-sensitive adhesive" as used in this Specification is meant a reaction product which remains tacky over a wide range of temperatures, viz. at least $-20°C.$ to $70°C.$, and which will adhere to most surfaces when light pressure is applied at ambient temperatures in the absence of heat, moisture and other agents.

The polyols employed in this invention may be hexols, e.g. sorbitol, pentols, e.g. arabitol, tetrols, e.g. pentaerythritol, or triols, e.g. glycerol. Also, reaction products of these polyols and propylene oxide and/or ethylene oxide may be used in place of the unmodified polyols, the preferred triol being a reaction product of glycerol and propylene oxide. Examples of diols which can be employed are poly(ethylene glycol) and poly(propylene glycol) which is the preferred diol. Examples of mono-ols which can be used are methyl oxitol and *n*-butanol.

Various combinations of hydroxyl-containing compounds, i.e. mono-ols, diols, triols, etc., can be employed in this invention, for instance, a single kind of tetrol or triol, mixtures of different tetrols and/or triols having different molecular weights, mixtures of

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one or more kinds of tetrol and/or triol and one or more kinds of diol, and mixtures of one or more kinds of tetrol and/or triol and one or more kinds of mono-ol. However, no matter what combination of hydroxyl-containing compounds is used, it is essential that the amounts used are such that when reacted with an organic polyisocyanate the average chain-length of the reaction product will be from 130 to 285 chain-atoms. For example, when a single triol of the glycerol/propylene oxide reaction product type is used, it should have a molecular weight of between about 4,000 and 8,000 when reacted with a low molecular weight polyisocyanate. This range will be lower if it is reacted with a high molecular weight polyisocyanate.

The average reaction product chain-length in terms of the number of atoms in the chain, which a particular polyol and a particular polyisocyanate will produce, is determined by the following method. As an example, a reaction product of glycerol and propylene oxide having a molecular weight of 5,000 is reacted with the stoichiometrical amount of 4,4'-diisocyanatodiphenylmethane. The average aggregate atomic weight of each arm of the triol is taken as $\frac{5,000}{3}$, i.e. 1,666. Each arm of the triol is taken as consisting of propylene oxide units

$$(\text{—CH(CH}_3\text{)—CH}_2\text{—O—})$$

and each unit has an aggregate atomic weight of 58 which is taken as being equivalent to only three atoms, viz., the chain-atoms,

$$\text{—C—C—O—}.$$

Therefore, the number of chain-atoms in each arm of a triol unit in the reaction product is $1,666 \times \frac{3}{58}$, i.e. 86. The 4,4'-diisocyanatodiphenylmethane units in the reaction product have the formula

$$\text{—CO—NH—C}_6\text{H}_4\text{—CH}_2\text{—C}_6\text{H}_4\text{—NH—CO},$$

for which the number of chain-atoms is taken as 11 (allowing three chain-atoms for each $\text{—C}_6\text{H}_4\text{—}$ group). Thus, each chain-length in the reaction product will have an average number of chain-atoms equal to $86+11+86$, i.e. 183. This method can be used in reverse to determine which polyol/polyisocyanate mixtures will produce a reaction product having an average chain-length of between 130 and 285 chain-atoms.

When one or more triols and one or more diols are reacted with an organic polyisocyanate, it is found that pressure-sensitive adhesives having more consistent properties are produced when the triols have low molecular weights, e.g. 100—500, and the diols have high molecular weights, e.g. 1,000—3,000.

When a mixture comprising at least one triol and at least one diol is used, the proportions which would theoretically give a poor pressure-sensitive adhesive, that is, one which is too hard, may in practice give a reaction product which exhibits good pressure-sensitive adhesive properties. This is owing to the existence of a variation in chain-lengths in the reaction product. Thus, a high proportion of chain-lengths having an average of from 130 to 285 chain-atoms may be produced from mixtures whose proportions would not be expected to produce a good pressure-sensitive adhesive if the resultant reaction product were ideal. By "ideal" is meant that all chain lengths in the reaction product are the same.

The organic polyisocyanate used in this invention may be aliphatic or aromatic, e.g. 4,4'-diisocyanatodiphenylmethane, 2,4- or 2,6-tolylene diisocyanate, hexamethylene diisocyanate, triphenylmethyl triisocyanate, 2,4,4'-triisocyanatodiphenylether and polymethylene-polyphenyl isocyanate.

Usually, an accelerator such as dibutyl tin dilaurate or stannous octoate is added to the reaction mixture prior to curing.

Also, if desired, an antioxidant can be incorporated into the reaction mixture prior to curing. This has the effect of stabilising the adhesive composition against loss of tackiness on exposure to air.

The pressure-sensitive adhesives of this invention are advantageous in that they do not need to be dissolved or dispersed in a solvent or dispersing agent, respectively, for application of the adhesive to a substrate, and the degree of tackiness and non-transferability of the adhesive do not change appreciably over a wide range of temperatures, viz. $-20°$C. to 120°C.

The invention is illustrated in the following Examples:—

Example I

In this Example, 10 gm portions of various triols of different molecular weights are individually mixed with 4,4'-diisocyanatodiphenylmethane in the presence of 0.1 gm of dibutyl tin dilaurate as accelerator, and it is shown that only the triols having molecular weights within the range calculated to produce reaction products having average chain-lengths of from 130 to 285 chain-atoms are suitable.

The amount of diisocyanate used in each case was the stoichiometrical amount calculated to react with all the hydroxyl groups present. Further details are given in Table I, in which the following abbreviations have been made for convenience:—

MW	=	Molecular weight of triol.
DDM	=	Amount of 4,4′-diisocyanatodiphenylmethane (gm)
RPCL	=	Average aggregate atomic weight of each chain-length in the reaction product
CLA	=	Number of atoms in each chain-length of the reaction product

TABLE I

	MW	DDM	RPCL	CLA
A	300	12.75	450	21
B	3000	1.28	2250	114
C	4000	0.953	2916	149
D	5000	0.75	3582	183
E	6000	0.625	4250	218
F	9000	0.425	6250	325

The triols used in this Example were all obtained commercially and were all reaction products of glycerol and propylene oxide except the triol of molecular weight 9000 which was a reaction product of glycerol and propylene oxide with an ethylene oxide unit at the end of each arm of the triol.

The RPCL and CLA values were calculated by the method hereinbefore described, the aggregate atomic weight of the propylene oxide units in each arm of the triol of molecular weight 9,000 being 3,000 minus the aggregate atomic weight of a triol ethylene oxide unit (—CH_2—CH_2—OH), i.e. 3,000—45, i.e. 2955, and the number of chain-atoms due to the two reaction product ethylene oxide units (—CH_2CH_2—O—) being 6, i.e. two units per chain.

The mixtures A—F were then cured. Mixture A cured at room temperature in a few minutes. Mixture B cured at room temperature slowly but cured at 70°C. in one hour. Mixtures C—E cured at 70°C. in one-and-a-half hours. Mixture F cured at 70°C. in two hours.

The properties of the resulting cross-linked reaction products are shown in Table II:—

TABLE II

A	—	Hard, brittle solid
B	—	Non-tacky, rubbery solid
C	—	Slightly softer and tackier than B
D	—	Soft, non-transferable, slightly tacky semi-solid (tack value = 217 gm)
E	—	Soft, non-transferable, tacky semi-solid (tack value = 45 gm)
F	—	Very soft, transferable, very tacky semi-solid

It was thus found that of the Mixtures A—F, only Mixtures C, D and E were suitable for use as pressure-sensitive adhesives.

The tack values of Mixtures D and E were measured at room temperature by a Dunlop Tackmeter (British Patent No. 741,214).

EXAMPLE II

This Example illustrates the preparation and properties of a pressure-sensitive adhesive prepared from a mixture of triols of different molecular weights. The triols used in this Example were reaction products of glycerol and propylene oxide.

A mixture of 10 gm of a triol of molecular weight 4,000, 10 gm of a triol of molecular weight 5,000, 20 gm of a triol of molecular weight 6,000, 2.99 gm of 4,4′-diisocyanatodiphenylmethane and 0.3 gm of dibutyl tin dilaurate, was cured at 70°C. for about one-and-a-half hours. The resulting cross-linked reaction product was fairly hard, showed no signs of transfer at 100°C. and had a tack value of 516 gm.

EXAMPLE III

This Example illustrates the preparation and properties of a pressure-sensitive adhesive prepared from a mixture comprising a triol and a diol.

Four mixtures, G—J, were prepared employing different triols and diols, shown in Table III, in which all parts are parts by weight.

In Table III, the following abbreviations have been made for convenience:—

5000T = Reaction product of glycerol and propylene oxide, having a molecular weight of 5000

300T = Reaction product of glycerol and propylene oxide, having a molecular weight of 300.

1500D = Poly(propylene glycol) having a molecular weight of 1500

2000D = Poly(propylene glycol) having a molecular weight of 2000

DDM = 4,4′-diisocyanatadiphenylmethane

DTD = Dibutyl tin dilaurate

TABLE III

	G	H	I	J
5000T	10	10	—	—
300T	—	—	1	1
1500D	2.5	—	11	—
2000D	—	2.0	—	11.5
DDM	1.2	1.0	3.1	2.7
DTD	0.1	0.1	0.1	0.1

Each of the Mixtures G—J was cured at 70°C. for one-and-a-half hours, to produce a slightly soft, tacky reaction product. The tack values for the reaction products of Mixtures G—J were 600 gm, 580 gm, 550 gm, and 770 gm, respectively. It was found that Mixtures I and J gave reaction products which were less tacky but more consistent in their properties when the preparations were duplicated, than were Mixtures G and H. None of the reaction products showed any signs of transfer at 100°C..

EXAMPLE IV

This Example illustrates the preparation and properties of a pressure-sensitive adhesive prepared from a mixture of a triol and a mono-ol.

Four mixtures, K—N, were prepared as shown in Table IV in which all parts are parts by weight.

In Table IV, the following abbreviations have been used for convenience:—

6000T, 5000T and 4000T = Reaction products of glycerol and propylene oxide, having molecular weights of 6000, 5000 and 4000, respectively

MO = Methyl oxitol

DDM and DTD = Same as for Table III

TABLE IV

	K	L	M	N
6000T	10	—	—	—
5000T	—	10	—	—
4000T	—	—	10	10
MO	0.005	0.028	0.010	0.020
DDM	0.64	0.80	0.96	0.97
DTD	0.1	0.1	0.1	0.1

The mixtures, K—N, were cured at 80°C. for one hour and the properties of the resulting reaction products are shown in Table V:—

TABLE V

K	—	Fairly hard, non-transferable, tack value = 380 gm.
L	—	Fairly soft, slightly transferable, tack value = 385 gm.
M	—	Fairly hard, non-transferable, tack value = 463 gm.
N	—	Fairly hard, non-transferable, tack value = 480 gm.

The tack values given in this Specification were measured at room temperature by a Dunlop Tackmeter (British Patent No. 741, 214).

WHAT WE CLAIM IS:—

1. A pressure-sensitive adhesive comprising a fully cross-linked reaction product of one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and an organic polyisocyanate, said reaction product having an average chain-length of from 130 to 285 chain-atoms.

2. An adhesive according to claim 1 which also comprises an antioxidant.

3. A method of preparing a pressure-sensitive adhesive comprising reacting one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and this stoichiometrical amount of an organic polyisocyanate, the hydroxyl-containing compounds being in sufficient proportions dependent on their molecular weights to produce a fully cross-linked reaction product with said polyisocyanate, said reaction product having an average chain-length of from 130 to 285 chain-atoms.

4. A method according to claim 3 wherein one or more triols are reacted with a poly-

isocyanate in the absence of any other polyol, diol and mono-ol.

5. A method according to claim 3 wherein a triol and a mono-ol are reacted with a polyisocyanate in the absence of any other polyol and diol.

6. A method according to claim 5 wherein the mono-ol is methyl oxitol.

7. A method according to claim 4, 5 or 6 wherein the triol is a reaction product of glycerol and propylene oxide having a molecular weight of from 4000 to 8000.

8. A method according to claim 7 wherein the molecular weight of the triol is 5000.

9. A method according to claim 3 wherein a triol and a diol are reacted with a polyisocyanate in the absence of any other triol or diol and mono-ol.

10. A method according to claim 9 wherein the triol has a molecular weight of from 100 to 500 and the diol has a molecular weight of from 1000 to 3000.

11. A method according to claim 9 or 10 wherein the triol is a reaction product of glycerol and propylene oxide.

12. A method according to claim 9, 10 or 11 wherein the diol is poly(propylene glycerol).

13. A method according to any one of claims 3 to 12 wherein the polyisocyanate is a diisocyanate.

14. A method according to claim 13 wherein the diisocyanate is 4,4′-diisocyanatodiphenylmethane.

15. A method according to any one of claims 3 to 14 wherein an antioxidant is incorporated in the reaction mixture.

16. A method according to any one of claims 3 to 15 wherein an accelerator is incorporated in the reaction mixture.

17. A method according to claim 16 wherein the accelerator is dibutyl tin dilaurate.

18. A method according to any one of claims 3 to 17 wherein the reactants are applied in a liquid state to a substrate whereon they react to form the pressure-sensitive adhesive.

19. A method according to claim 3 and substantially as described in any of the foregoing Examples.

20. A pressure-sensitive adhesive when prepared by the method of any one of claims 3 to 19.

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Agent for the Applicants.

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